

Formation of ordered and disordered dielectric/metal nanowire arrays and their plasmonic behavior.

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ABSTRACT

We have recently shown that dielectric/metal composite nanowires can exhibit very strong surface enhanced Raman (SERS) signals, when arranged in a random 3D geometry. Since we believe that the intersections of nanowires are critical in generating the high electric fields necessary for this enhancement, we are investigating this effect under more controlled conditions. Thus, we will discuss the formation of nanowire arrays by in-situ growth, achieved by the control of nanowire material/substrate combination, as well as ex-situ nanowire array formation involving e-beam lithography. The effects of nanowire geometry and the resulting SERS behavior show the importance of the dielectric/metal configuration, as well as the importance of nanowire geometry in the SERS effect.

Keywords: Dielectric and semiconductor nanowires, VLS growth, Raman spectroscopy, SERS

1. INTRODUCTION

Optically based sensing provides advantages over electronic sensing because optical spectra can uniquely finger print a chemical compound, eliminating false alarms and simplifying the detection process. In addition, light can also be easily directed over long distances, enabling remote sensing. In Raman scattering (RS), light is scattered from a chemical of interest, and the vibrational modes in the chemical red shift the frequency of the scattered light, producing a spectrum of lines that are characteristic of that molecule. Since this fingerprint is unique to a given material, precise chemical identification is possible.

A major issue for ordinary Raman scattering is that its cross-sections are very small resulting in low sensitivity (1E-8 of the exciting laser). However, the Raman signal can be enhanced by many orders of magnitude by the use of metal nano-particles [1] and metal shell/dielectric core nano particle composites [2]. This enhancement is thought to be the result of local electromagnetic fields that are created by the laser excitation of surface plasmons at the metal surface. Even though

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enhancements as high as 1E8 to 1E12 have been reported for different nanostructures [3], the underlying mechanisms are not fully understood. This is evidenced by theoretical calculations which predict SERS enhancements that are many orders of magnitude greater than have been experimentally attained [2].

Thus, understanding the SERS mechanism and how it relates to the geometric properties of a SERS substrate is critical to any possible future applications in highly efficient sensors and taggants. This information is also required for the reproducibility of the enhanced signal and the reliability of SERS surfaces. Current research with metallic nanoparticles suggests that the size, geometry, shape, alignment and chemical effects are important parameters in the SERS effect [4-6]. For example, it has been shown that Au nanorods exhibit a stronger SERS effect than Au nanoparticles [7], and the plasmon resonance and the strength of the electric field can be tuned in a dielectric core/metal shell nanosphere geometry [2], as well as in metal/dielectric nanodisks [8]. In addition, special alignment also resulted in higher SERS intensity [9], as well as close proximity of the nanostructures to each other [2,10].

In view of the above results, we have developed a highly sensitive SERS substrate based on a random distribution of dielectric core/metal shell nanowire geometry [11,12], which can reliably detect 0.2 pgm of Rhodamine 6G (a standard SERS-active dye). The SERS enhancement for these experiments was greater than 10^8 , with the fluorescence being 3-5 orders of magnitude greater [12]. We believe that the random distribution of Ag/dielectric nanowires is important, because it maximizes the density of hot spots (high electric field regions) and allows molecules more access in depth than nanoshell geometries.

In order to elucidate the role of hot spots and their correlation to nanowire geometries, we have investigated various nanowire geometries, including random, parallel and nearly crossed arrays, as well as e-beam lithographically produced metallic lines, and we have investigated the strength of the SERS effect as a function of the various geometries, using our μ -Raman system. The results show the importance of cross-over geometry to maximize the SERS effect, as well as the importance of the dielectric core/metal sheath geometry.

2. EXPERIMENTAL PROCEDURES

Several different nanowire systems have been grown, including random Ga_2O_3 nanowires, InAs nanowires, ZnO nanowires, as well as Au lines produced by e-beam lithography. The growth of the Ga_2O_3 nanowires was achieved by the controlled oxidation of pure Ga metal in a vacuum tube furnace [13]. The source material was placed at one end of a 4" alumina boat, with the substrate at the opposite end. The boat was then inserted into a quartz tube inside a tube furnace, which was evacuated to a base vacuum of 40 mTorr using a mechanical pump. The furnace was then heated to 900°C. Several gas feed valves and flow controllers were connected to the other end of the tube, allowing a controlled flow of argon and oxygen gas to pass over the alumina boat. During the heat up cycle, the evacuated quartz tube was flushed several times with argon gas in order to reduce the initial oxygen content. Once at temperature, the growth was initiated by the flow of a 6:1 ratio of argon to oxygen. The InAs nanowires were grown inside a sealed quartz tube in an open tube furnace, as described previously [14]. The InAs substrates were first etched in HCl to remove any native oxide, and then gold colloid (Ted Pella, Inc.) drops were placed on the growth substrate, using poly L-lysine, which allows the deposition of a uniform distribution of gold nanoparticles on the surface. The substrate was immediately loaded, along with a bare InAs source substrate, inside a

quartz tube, which was evacuated to 70 mTorr and sealed with a torch. The center of the furnace was raised to the growth temperature, which ranged from 400°C to 660°C. The ZnO nanowires were grown at 550°C in a tube furnace under atmospheric conditions [12], using Zn pellets (Alpha-Aesar) as the source material. No metal catalyst was used for the growth of the ZnO nanowires. Finally, Au lines, having 50, 70, 90 and 110nm thick, with 186nm spacing, were produced by e-beam lithography. Two types of wires were fabricated, those that were only 20nm high and those which were 65nm high. All the grown nanowires were analyzed using a LEO SUPRA 55 scanning electron microscope (SEM), JEOL 2010F 200 KV high resolution transmission electron microscope (HRTEM) and X-ray energy dispersive spectroscopy (EDS) attached to the HRTEM, as well as Raman spectroscopy.

3.1 GROWTH OF NON-INTERACTING AND CROSSED InAs NANOWIRE ARRAYS

An image of the nanowires grown inside the sealed quartz tube 60nm gold colloids on Si(111) and SiO₂, respectively, is shown in Fig. 1a,b. Note that the nanowires are of uniform diameter, corresponding to the specific gold colloid size used. Each nanowire terminates with an Au-In colloid tip, as would be expected from the VLS mechanism,

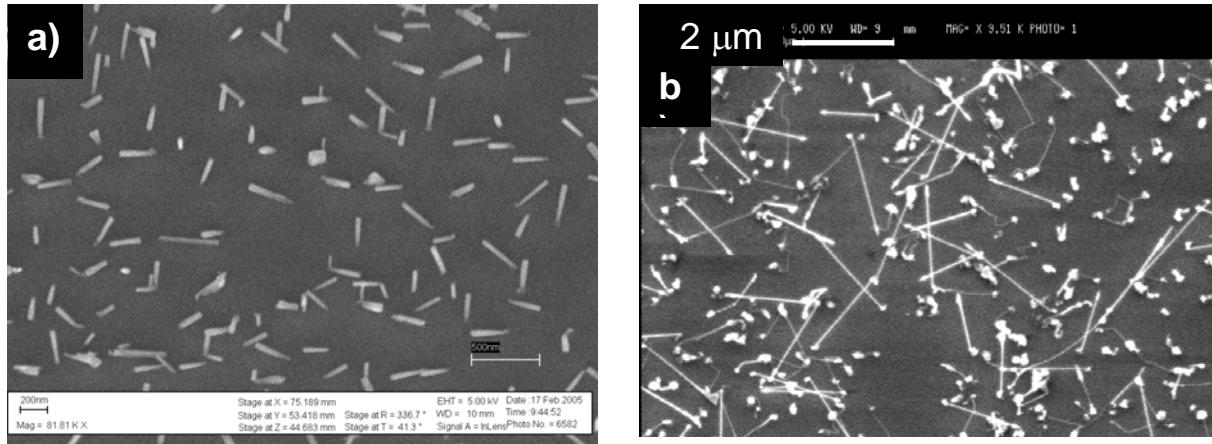


Figure 1: Growth of 60nm InAs nanowire arrays on a) Si(111) substrate and b) SiO₂ substrate.

From HRTEM results, the measured lattice spacing along the (111) direction is 0.344 nm, corresponding to the lattice spacing of bulk InAs. HRTEM EDS performed on the nanowire is indicated equal atomic percent of In and As, confirming stoichiometric InAs [14]. InAs nanowires which were grown on other substrates, such as Si(111) and SiO₂ also exhibited single crystal character and uniform size, but differing geometric placements, as shown in Figure 1. The nanowires grown on Si(111) were randomly oriented, exhibiting no symmetry with the substrate, but not interacting, while those grown on the oxide exhibited cross-over points.

3.2 GROWTH OF CLOSELY-SPACED PARALLEL ZnO NANOWIRES AND CROSSED Ga₂O₃ NANOWIRES.

As discussed above, due to the far separation of the gold colloid catalyst in the growth of the InAs nanowires, the resultant nanowire spacing is quite large, resulting in totally isolated nanowires for shorter growth times. In order to examine more closely spaced parallel nanowires, we have chosen the ZnO system, which does not require the use of a gold colloid for the nanowire growth, and thus results in more closely spaced wires. The result of this self-catalyzing growth mode for ZnO nanowires is shown in Figure 2a, along with a similar density of randomly crossed Ga₂O₃ nanowires, shown in Figure 2b. As can be seen, the ZnO nanowires nucleate in star-burst type patterns, only resulting in close parallel spacing of the nanowires near the origin. The farther away from the origin, the farther apart are the wires. In the case of the Ga₂O₃ nanowires, random crossings are evident everywhere.

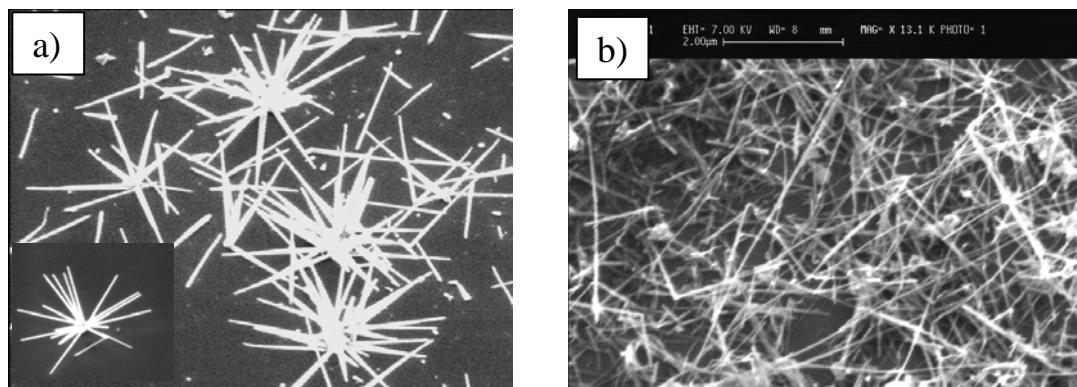


Figure 2. SEM image of single crystal ZnO nanowires in closer parallel geometry a) and b) Ga₂O₃ nanowires arranged in a random cross-over geometry.

3.3 FABRICATION OF Au PARALLEL LINES USING e-BEAM LITHOGRAPHY

In order to investigate the dependence of the SERS signal on the volume of Au, we have also examined thin and thick Au lines fabricated by e-beam lithography. A set of Au lines having widths of 70nm, 80nm, 95 nm and 110nm and thickness of 20nm or 65nm were fabricated, and SEM images of the 80nm and 95 nm Au line arrays are shown in Figure 3a,b.

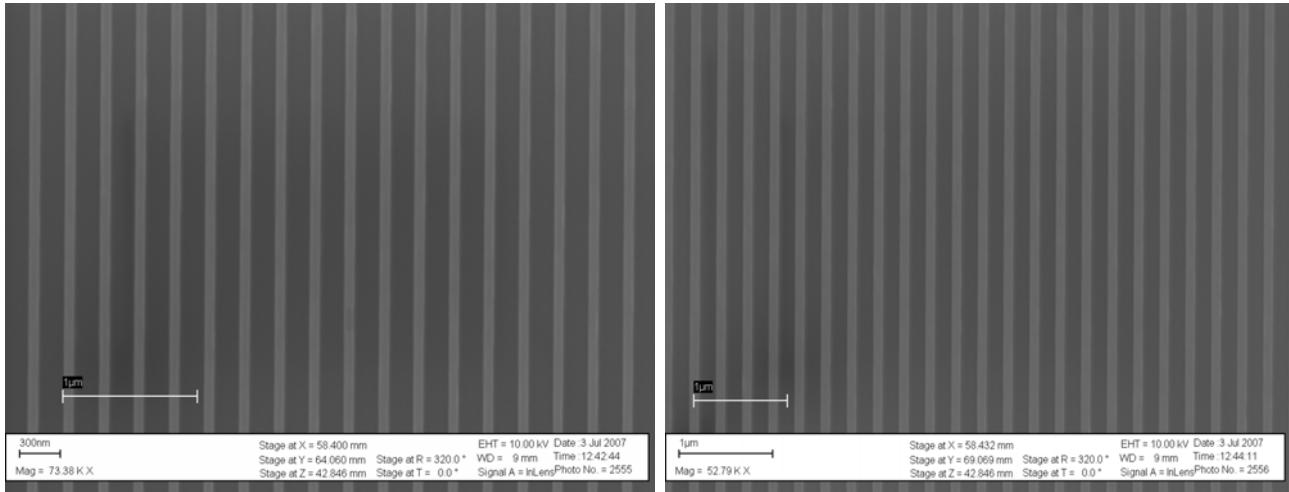


Figure 3. Lithographically produced Au lines of 80 nm and 95nm widths.

4. PLASMONIC PROPERTIES NANOWIRE COMPOSITE ARRAYS

We have previously shown that $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowire composites can be very efficient SERS substrates [11,12], and we have suggested that the nanowire crossings result in “hot” spots [12] in the electric fields, thus enhancing the SERS signal. Since we could not control the random array geometry in the Ga_2O_3 nanowire case, it was not possible to examine this concept in more detail. However, as shown above, we are now able to grow a variety of nanowire geometries, based on both in-situ growth of different nanowire systems, as well as the e-beam fabrication of Au lines. Thus, tailoring the geometries lets us investigate the “hot” spot concept even further.

In order to compare to the previous results, we have used 10^{-6} M Rhodamine 6G (RH6G) for these studies, and all the nanowire arrays were covered with a 5 nm layer of Ag, creating dielectric or semiconductor/Ag nanowire composites. The Ag film on a flat substrate did not exhibit any SERS signal, which rules out the effect of Ag roughness as the source of the SERS signal. In case of the InAs nanowire SERS substrate design, 60 nm InAs nanowires were produced using 60nm Au particle colloids, as shown in Figure 1. The first array involved the formation of random InAs nanowires on Si (111), which did not exhibit crossings, while the second set of nanowires were grown on SiO_2 , resulting in crossed, flat, random arrays, similar to those seen in the Ga_2O_3 nanowire system.

A comparison of the SERS signal, using the Rh6G molecule and the 5145nm line of the Ar ion laser at less than 1 mW of power, is shown in Figure 4. The most obvious result is that the crossed array geometry shows a SERS signal typical for Rh6G, while the non-crossing geometry exhibits no SERS. In addition, a very strong surface enhanced fluorescence (SEFs) is also evident (not shown) for the crossed wires, characterized by the broad, intense luminescence centered near 1500 cm^{-1} . The non-interacting wire arrays in Figure 1a do not exhibit the characteristic SERS of Rh6G, nor is a SEFs signal evident. In both cases, a similar nanowire density was measured, ruling out a simple volume effect. These results suggest the importance of cross-over geometry in order to achieve a significant SERS enhancement, which is a result of the very high electric fields which can be achieved in this type of geometry.

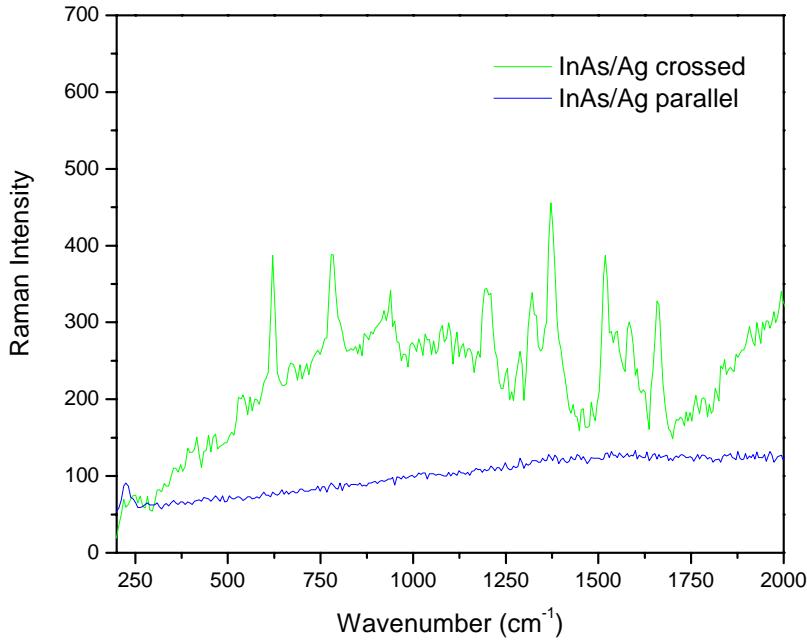


Figure 4: Comparison of the Raman spectra for crossed and parallel InAs/Ag nanowire composite arrays.

The importance of plasmon coupling at nanowire crossings can be seen in Figure 5a, which is a result of a finite element simulation [12] of the electric field near two obliquely crossed nanowires separated by 10 nm in air, in response to 500nm wavelength light polarized in the x-direction. An enhanced plasmon resonance is found in the vicinity of the crossing. However, the field maximum no longer occurs halfway between the closest separations between the wires, as in the parallel wire case. Instead, the maximum is displaced away from the crossing angle, in a much larger volume

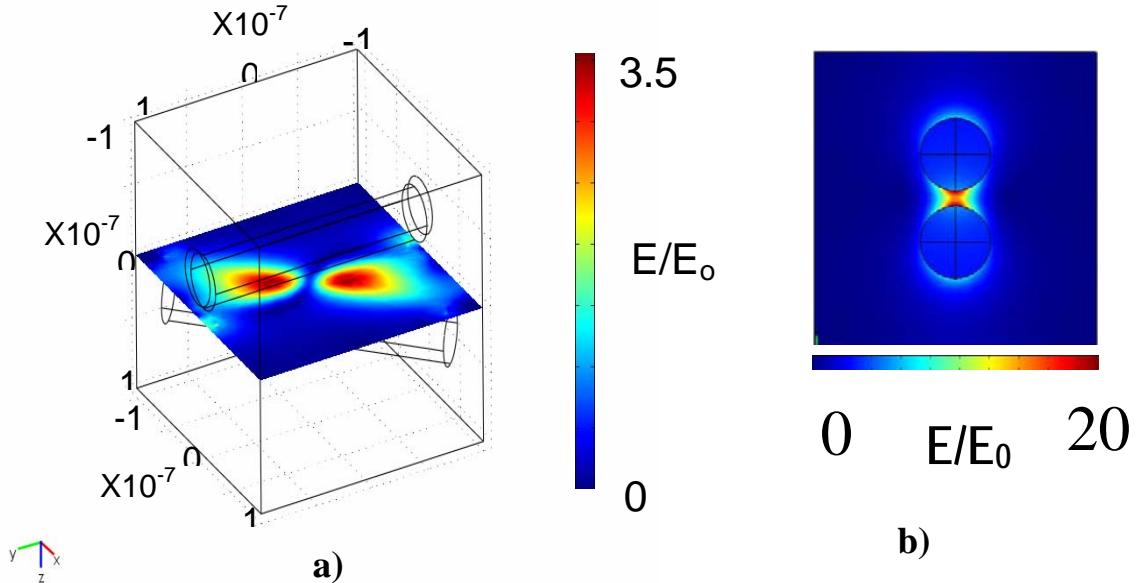


Figure 5. COMSOL electric field calculation of crossed nanowires a) and closely spaced nanospheres which exhibit maximum electric field enhancement for spacing of $< 2\text{nm}$ b).

surrounding each crossing. This would not only enhance the SERS effect due to the strong coupling, but allow more molecules to enter this high electric field region, thereby enhancing the SERS sensitivity. Furthermore, the parallel wire geometry [15], as well as nanosphere geometries, requires a very specific spacing in order to maximize the enhancement due to coupling, as shown in Figure 5b. This is not the case in crossed wires, since an optimal spacing will always be present for every crossing angle due to the wire geometry. Randomly crossed wires would be expected to exhibit two such maxima in the vicinity of each of the crossings, as shown in Figure 5a.

The advantage of plasmonic coupling can be thus examined if one now considers the SERS results for the two different geometries shown in Figure 2. In this case, the ZnO/Ag nanowires

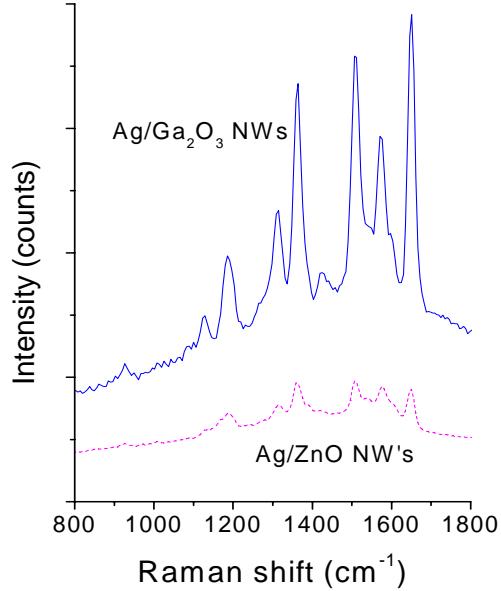


Figure 6. SERS results of ZnO/Ag nanowire composites and Ga_2O_3 /Ag nanowire composites.

exhibit close, nearly parallel spacing near the origin, while the random Ga_2O_3 /Ag nanowire composites exhibit a high density of oblique crossings throughout the array. A comparison of the SERS signal is shown in Figure 6. As can be seen, although the ZnO nanowire composites do exhibit a SERS signal, it is significantly weaker than that from the Ga_2O_3 /Ag nanowire composites. This can be understood from the perspective of Plasmon coupling, since one would expect much greater coupling in the case of the highly crossed wires.

The importance of the nanowire crossings can be even more obvious if one considers a single nanowire system, as shown in Figure 7. In this case, the laser line was scanned across the nanowire in a horizontal direction, marked as 1, as well as a vertical direction, marked as 2, shown in an optical image in Figure 7a. The corresponding SERS spectra are shown in Figure 7b,c, respectively. What is quite evident is that in the horizontal direction, very little SERS signal is evident as a function of distance across the wire, while in the vertical direction, a strong SERS signal for RH6G can be seen as the wire is intersected. The reason for this surprising difference becomes quite clear when this specific nanowire is examined in SEM, which allows for a more detailed examination of the nanowire structure and geometry (shown in Figure 7d). As can be seen, the horizontal scan involves only the intersection of the single large nanowire, while the vertical scan results in the

intersection over a nanowire crossing, as marked in the Figure 7d. Thus, in this case, the crossing of the two nanowires leads to significantly enhanced plasmon coupling, and thus to much enhanced electric fields and a much stronger SERS, as predicted from the finite element analysis.

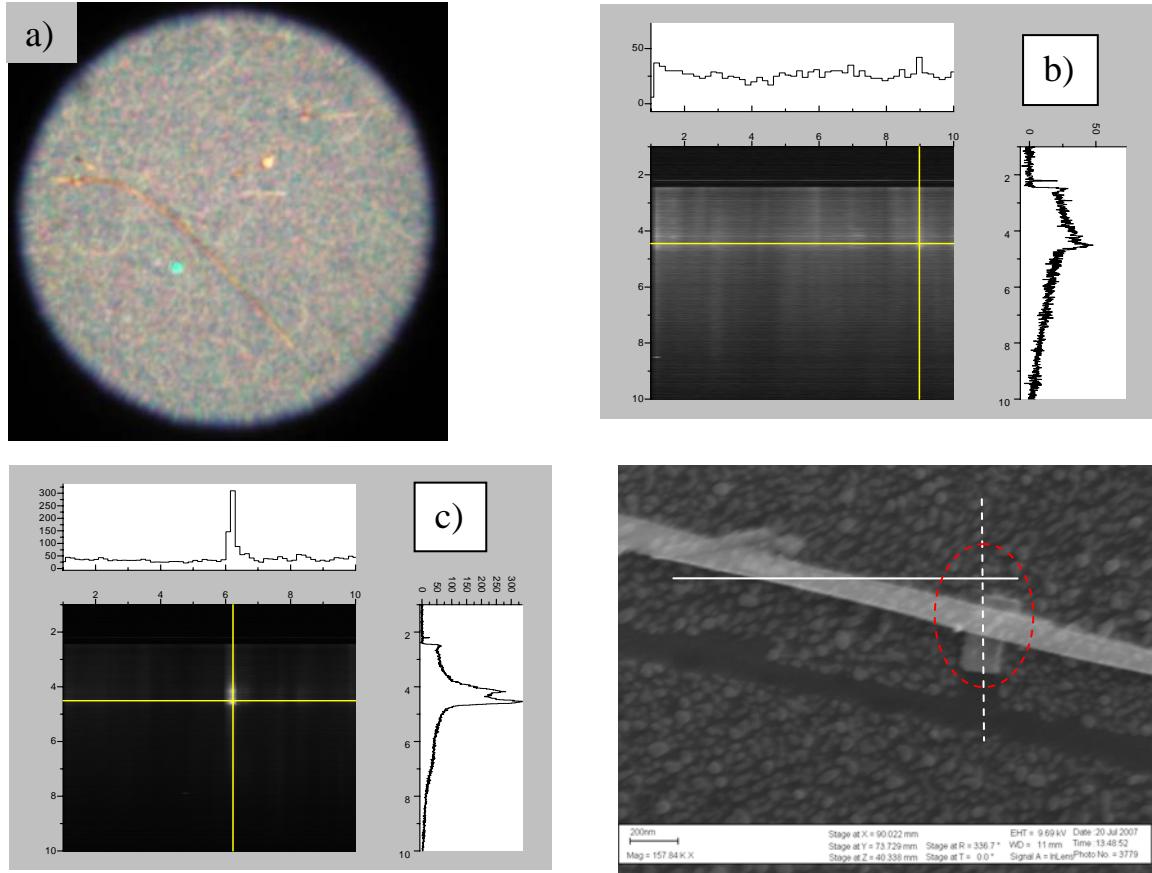


Figure 7. Optical micrograph of a Ga_2O_3 nanowire indicating the scan direction of lasers line a) and b) SERS spectra for horizontal and vertical laser scan, and d) SEM micrograph of actual nanowire geometry, showing the crossing of two wires.

A more ordered nanowire structure can also be produced by e-beam lithography, as shown in Figure 3. In this case, both 80nm and 95nm Au lines, with 186nm separation, were produced and examined for SERS using 10^{-6}M Rhodamine 6G solution. The SERS results are shown in Figure 8, and both structures exhibit SERS for Rh6G, with the 95nm lines showing slightly stronger SERS signal. Interestingly, when identical thickness Au lines, having only 20nm thickness, were examined, no SERS signal was evident. This suggests that the required dimensions for effective SERS are really in 3D and not just in 2D. examined for SERS using 10^{-6}M Rhodamine 6G solution. The SERS results are shown in Figure 8, and both structures exhibit SERS for Rh6G, with the 95nm lines showing slightly stronger SERS signal. Interestingly, when identical thickness Au lines, having only 20nm thickness, were examined, no SERS signal was evident. This suggests that the required dimensions for effective SERS are really in 3D and not just in 2D.

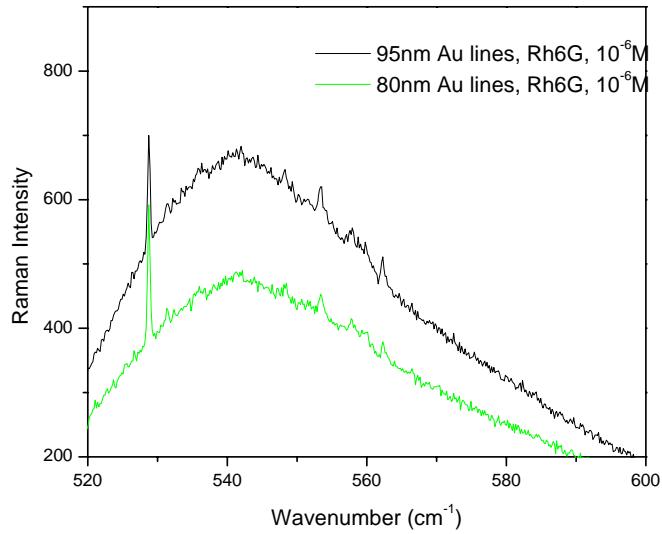


Figure 8. SERS signal for 95nm and 80nm Au lines produced by e-beam lithography. The molecule used for 10^{-6} M Rh6G.

Since the Au lines are spaced 186nm apart, one would not expect effective plasmon coupling between the wires, and thus the SERS signal is rather weak. We can, however, examine the effect of local geometry by the use of Au lithographically produced lines, and a solution of the $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowire composites. In this case, in order to reduce the fluorescence, we have chosen to use benzene thiol (BZT), which does not experience excitation using the 5145nm laser line. However, BZT is not as easily detected using SERS. Thus, no SERS was detectable for the Au lines only, as shown in figure 9a,b. If $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowires are subsequently deposited on the substrate containing the 95nm Au lines, a number of nanowire geometries can be seen, as shown in Figure 10a,b.

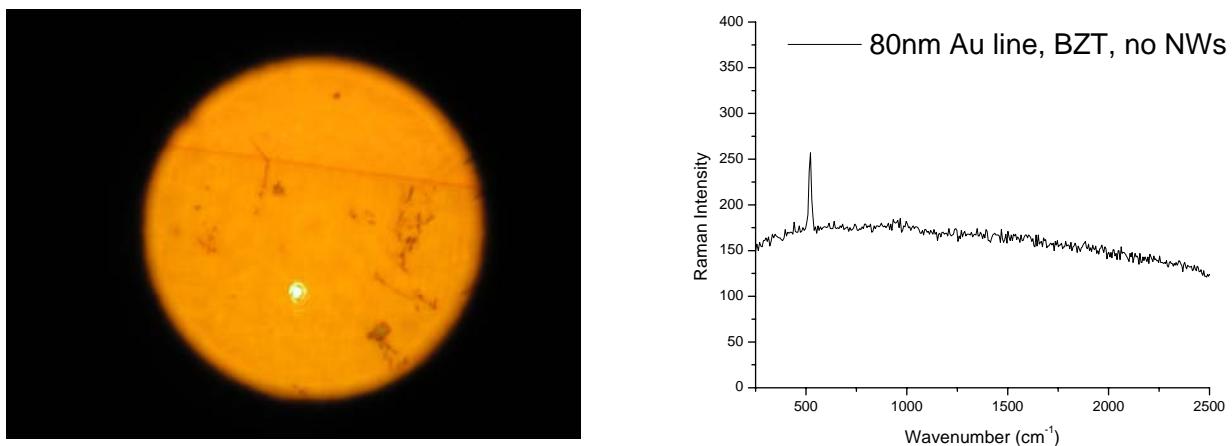


Figure 9. Optical image of a nanowire-free region of the 95nm Au lines (a) and (b) SERS signal from this region. The peak near 520cm^{-1} is due to the Si substrate

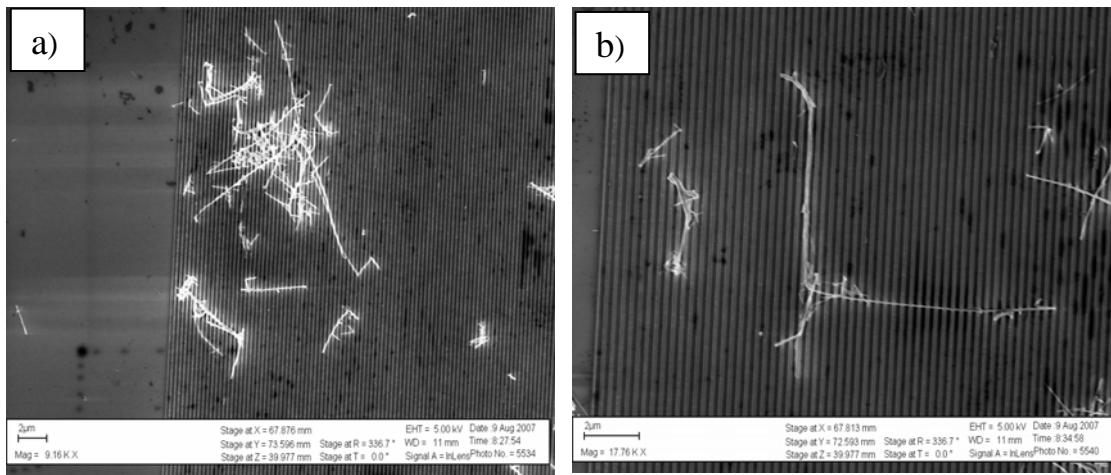


Figure 10. SEM images of a) clump of nanowires and b) nanowire "T" placed on top of 95nm Au lines.

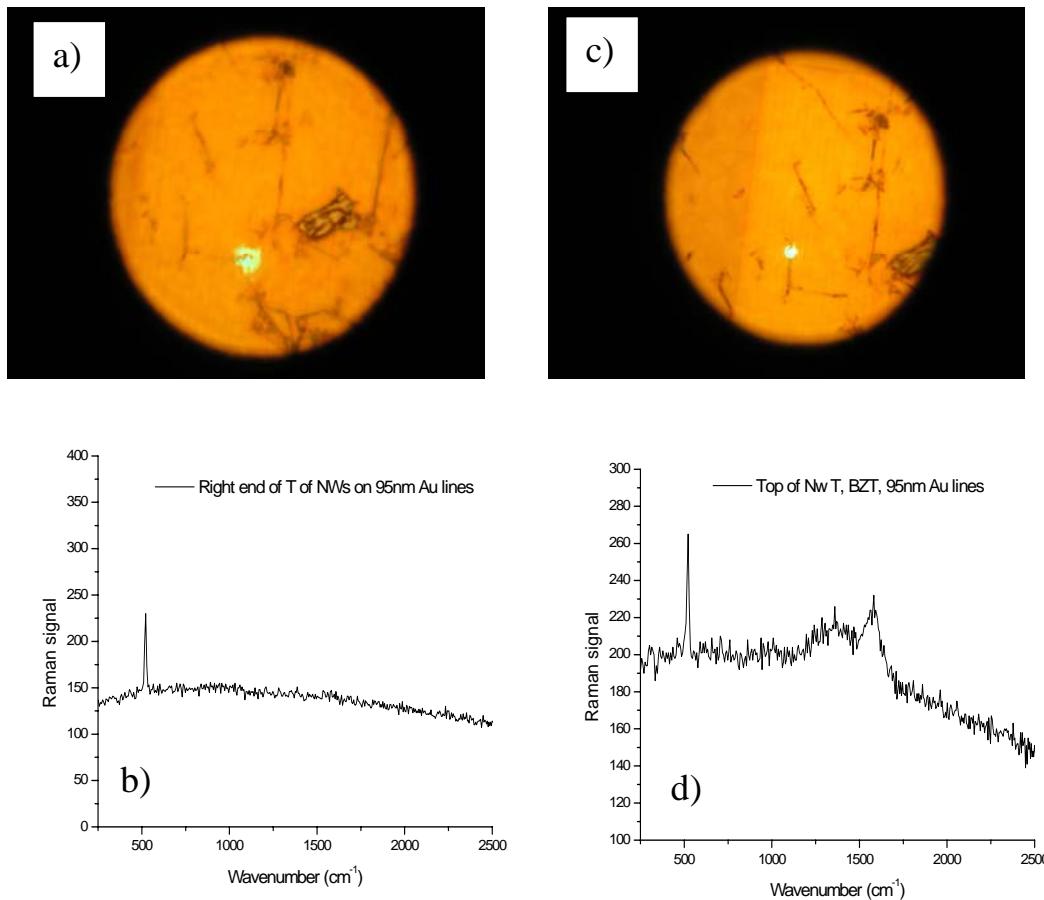


Figure 11. Optical images and corresponding SERS spectra of a NW perpendicular (a,b) and parallel (c,d) to the Au lines.

The interesting aspect of this type of geometry is that the “T” formation shown in figure 10b allows for the measurements of SERS using a nanowire which is parallel or perpendicular to the underlying Au lines. An optical image of the two locations where SERS was obtained, along with the spectral images, is shown in Figure 11. As is evident, the perpendicular wire does not show any SERS for the BZT while the parallel line has a noticeable SERS signal. In order to understand this result, let us briefly consider the expected SERS enhancement for wires as a function of angle between each other obtained from the COMSOL simulation, shown in Figure 12, as well as the actual geometry, as determined from SEM, also shown in Figure 12.

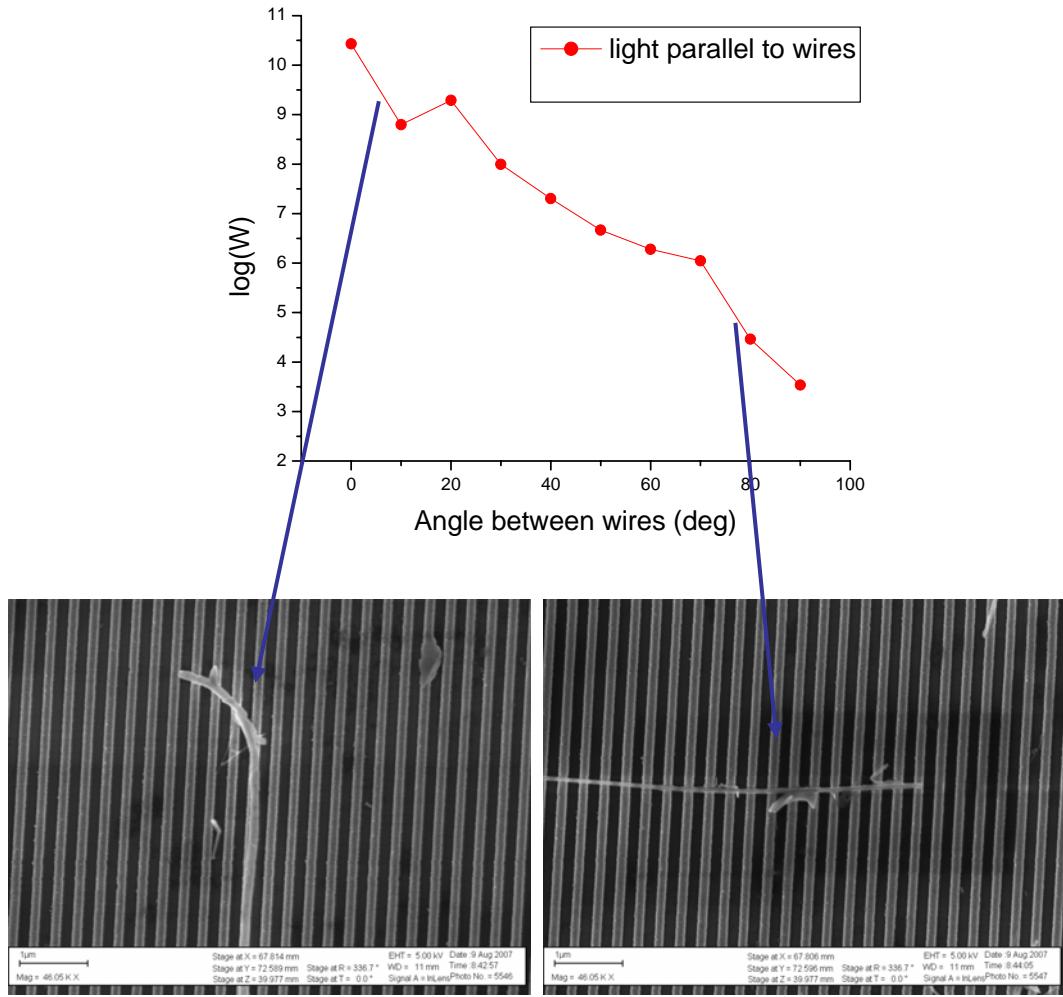


Figure 12. COMSOL calculation of the expected SERS enhancements for wires as a function of crossing angle and SEM images of the parallel and perpendicular wires in the “T” configuration.

As can be seen from the simulation, one would expect a much larger enhancement from nanowires which are nearly parallel and very closely spaced, as is evident from the SEM image of the parallel wire. The perpendicular wire should exhibit much lower enhancement in this geometry, which is confirmed by the data in Figure 11, in which the parallel nanowire geometry exhibits a noticeable SERS while in the perpendicular case no SERS is evident.

5. CONCLUSION

In conclusion, we have addressed the effect of geometry on the electric field enhancement in the SERS effect, using a variety of dielectric or semiconductor/metal nanowire composites, as well as Au lines produced by e-beam lithography. By appropriate choice of growth mechanism and substrate, we were able to produce nanowires which exhibit different array geometries. In this way, we have been able to grow non-interacting nanowire arrays, as well as flat, crossed arrays, which show significantly different SERS results using Rh6G as the sensing molecule. These results indicate that a crossed geometry leading to electric field “hot” spots can significantly enhance the SERS signal from target molecules, as well as very closely spaced parallel nanowires. SERS measurements using Rhodamine 6G have shown these substrates to be highly sensitive, and it is suggested that this enhancement is the results of both the dielectric core/metal shell geometry and the formation of a large number of “hot” spots when arranged in an appropriate geometry. Finite element calculations show significantly enhanced electric fields in the regions of the wire crossing, in support of the experimental results.

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